Critical Research for Cost-effective Photoelectrochemical Production of Hydrogen

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This presentation does not contain any proprietary or confidential information

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170-PDP-35

THE UNIVERSITY OF TOLEDO

National Renewable Energy Laboratory
A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Innovation for Our Energy Future

United Solar Ovonic

Overview

Timeline

- Project start date: 10/13/2004
- Project end date: 10/12/2007
- Percent complete: 1%

Budget

- Total project funding
  - DOE share: $2,921,501
  - Contractor share: $760,492
- Funding received in FY04 to date : 0
- Funding for FY05: ?

Barriers addressed

- DOE MYPP Objective for PEC
  - By 2015, demonstrate direct PEC water splitting with a plant-gate hydrogen production cost of $5/kg projected to commercial scale.
- Technical Targets:
  - 2010: STH Eff >9%;   Durability >10,000 hours; Cost < $22/kg
  - 2015: STH Eff >14%; Durability >20,000 hours; Cost < $5/kg
- PEC Hydrogen Generation Barriers -- MYPP 3.1.4.2.3
  - M. Materials Durability
  - N. Materials and Systems Engineering
  - O. PEC efficiency

Partners

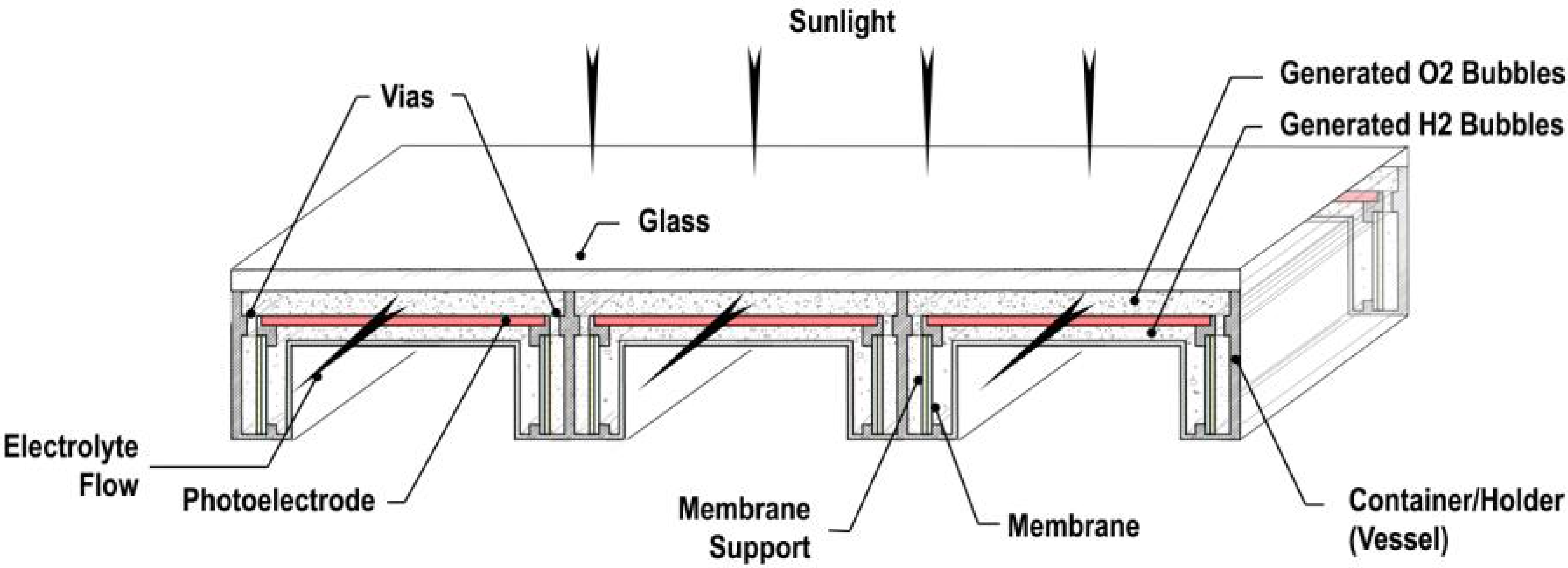
- University of Toledo
- National Renewable Energy Laboratory
- United Solar Ovonic Corp.

Objectives

- To develop critical technologies required for cost-effective production of hydrogen from sunlight and water using thin film-Si based photoelectrodes.

- To develop and demonstrate, at the end of the 3-year program, immersion-type tf-Si based PEC systems with 9% solar-to-hydrogen efficiency with a lifetime of 10,000 hours and with a potential hydrogen cost below $22/kg.

Approach - PEC cell

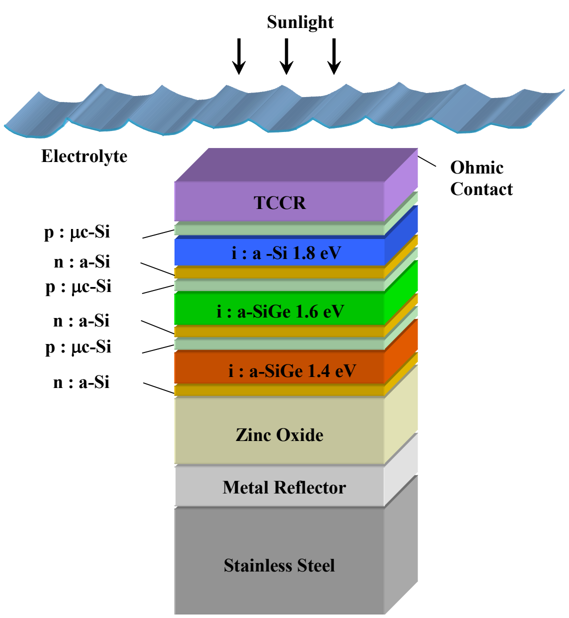


Approach - PEC electrode

Two separate approaches for the development of high-efficiency and stable PEC photoelectrode:

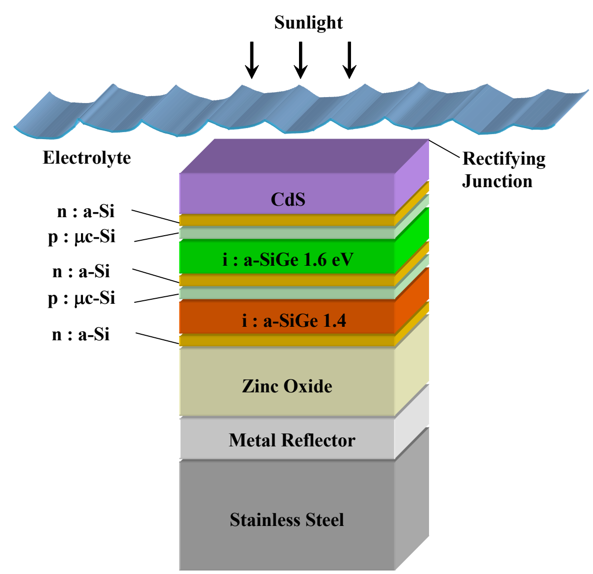
Approach 1 (Task 1):

- Develop triple junction tf-Si photoelectrodes covered with a transparent, conductive, and corrosion resistant (TCCR) protection layer



Aproach 2 (Task 2):

- Develop hybrid, triple junction photoelectrodes with a semiconductor-electrolyte junction as the top junction and tf-Si alloys as the middle and bottom junctions



Approach - Tasks

- Task 1: Transparent, conducting and corrosion resistant coating for triple-junction tf-Si based photoelectrode
- Task 2: Hybrid multijunction PEC electrode having semiconductor-electrolyte junction
- Task 3: Understanding and characterization of photoelectrochemistry
- Task 4: Fabrication of low-cost, durable and efficient immersion-type PEC cells and systems
- Task 5: Fabrication of 8ft^2, substrate-type PEC panels

Progress/Results

DC Magnetron Sputter Deposition of TiO_2, Fe_2O_3 and WO_3

- Completed the construction of two new sputter deposition chambers for oxides depositions, with each chamber having three sputter targets capable of depositing from three different sources simultaneously
- Deposited TiO_2, Fe_2O_3 and WO_3 films.
- For TiO_2, deposited films with
  - different oxygen content
  - different nitrogen doping
  - different indium doping

Deposition Conditions for TiO_2 films

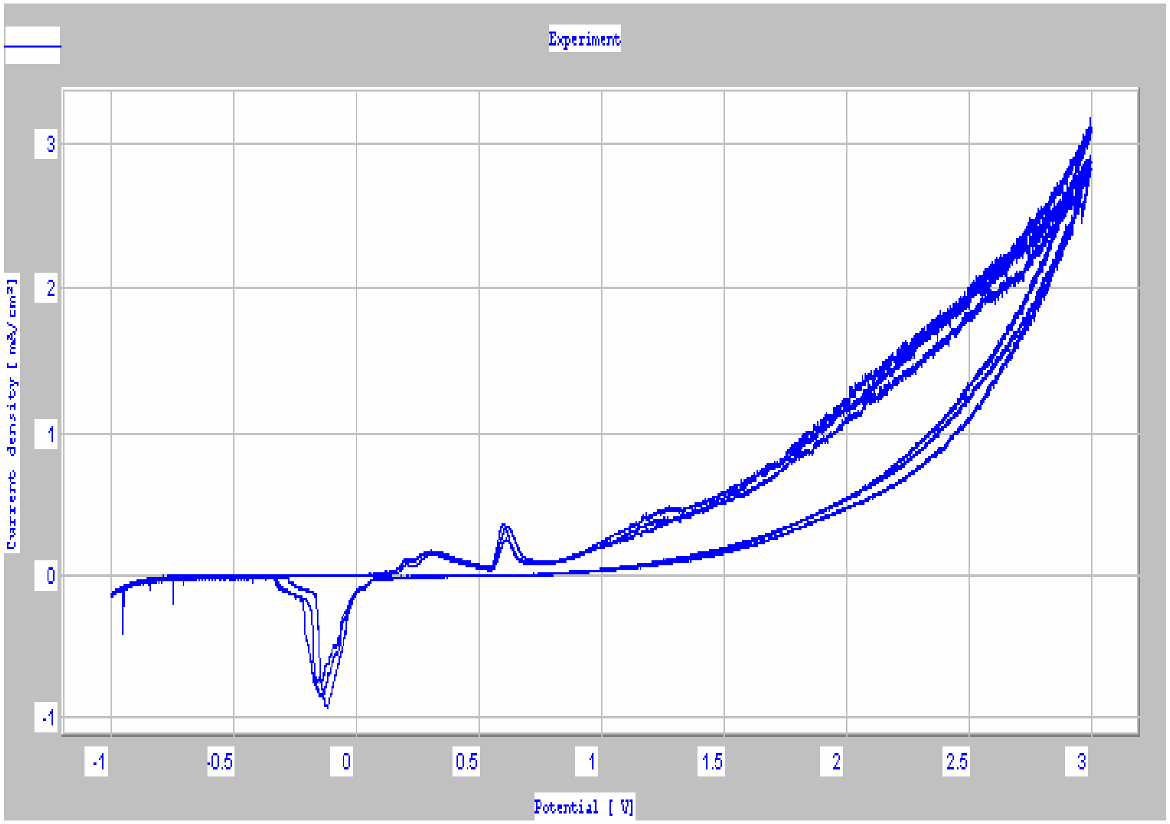
Sample	Power (W)	Time (min)	Temp (°C)	Pressure (mTorr)	Atmosphere	Comments
ST005	50	60	200	4	Ar	NONE
ST006	50	60	250	4	Ar	NONE
ST007	50	60	300	4	Ar	NONE
ST008	50	60	150	4	Ar	NONE
ST009	40	100	200	4	Ar	NONE
ST010	40	100	250	4	Ar	NONE
ST011	40	100	300	4	Ar	NONE
ST012	40	100	150	4	Ar	NONE
ST013	60	60	200	4	2% O_2, Ar	NONE
ST014	60	60	250	4	2% O_2, Ar	NONE
ST015	50	80	200	4	2% O_2, Ar	NONE
ST016	40	100	200	4	2% O_2, Ar	NONE
ST017	60	180	200	4	2% O_2, Ar	NONE
ST018	30	120	200	4	2% O_2, Ar	NONE
ST019	40	100	250	4	2% O_2, Ar	NONE
ST020	50	80	250	4	2% O_2, Ar	NONE
ST021	60	200	200	4	2% O_2, Ar	NONE
ST022	40	100	150	4	2% O_2, Ar	NONE
ST023	50	80	150	4	2% O_2, Ar	NONE
ST024	40	300	200	4	2% O_2, Ar	NONE
ST025	40	120	200	4	5% O_2, Ar	NONE
ST026	40	120	250	4	5% O_2, Ar	NONE
ST027	50	120	200	4	5% O_2, Ar	NONE
ST028	50	120	250	4	5% O_2, Ar	NONE

Sample	Power (W)	Time (min)	Temp (°C)	Pressure (mTorr)	Atmosphere	Comments
ST029	60	120	200	4	5% O_2, Ar	NONE
ST030	60	120	250	4	5% O_2, Ar	NONE
ST031	60	180	200	2	5% N_2 Ar	NONE
ST032	70	180	200	2	5% N_2 Ar	NONE
ST033	80	60	200	4	5% N_2 Ar	NONE
ST035	90	60	200	4	5% N_2 Ar	NONE
ST042	80	60	200	4	2% O_2, Ar	In, 10 W
ST043	90	60	200	4	2% O_2, Ar	In, 10 W
ST045	90	60	200	4	2% O_2, Ar	In, 15 W
ST046	90	60	200	4	2% O_2, Ar	In, 20 W
ST047	80	60	200	4	30% N_2 Ar	NONE
ST048	90	60	200	4	30% N_2 Ar	NONE
ST049	80	60	250	4	30% N_2 Ar	NONE
ST050	90	60	250	4	30% N_2 Ar	NONE
ST051	100	60	200	4	30% N_2 Ar	NONE
ST052	100	60	200	4	2% O_2, Ar	In, 15 W
ST053	100	60	200	4	2% O_2, Ar	In, 20 W
ST054	100	60	200	4	2% O_2, Ar	In, 10 W
ST056	100	60	200	4	2% O_2, Ar	In, 7 W
ST057	100	120	200	4	2% O_2, Ar	In, 15 W
ST059	100	120	250	4	2% O_2, Ar	In, 15 W
ST060	100	120	250	4	Ar/N2: 8/5 sccm	NONE
ST062	100	120	250	4	Ar/N2: 8/5 sccm	4h anneal

TiO_2

- I-V curve for TiO2 shown in figure.
- Addition of small amounts of O_2 during TiO2 deposition improves film's electrochemical stability

Current Density (mA/cm^2)

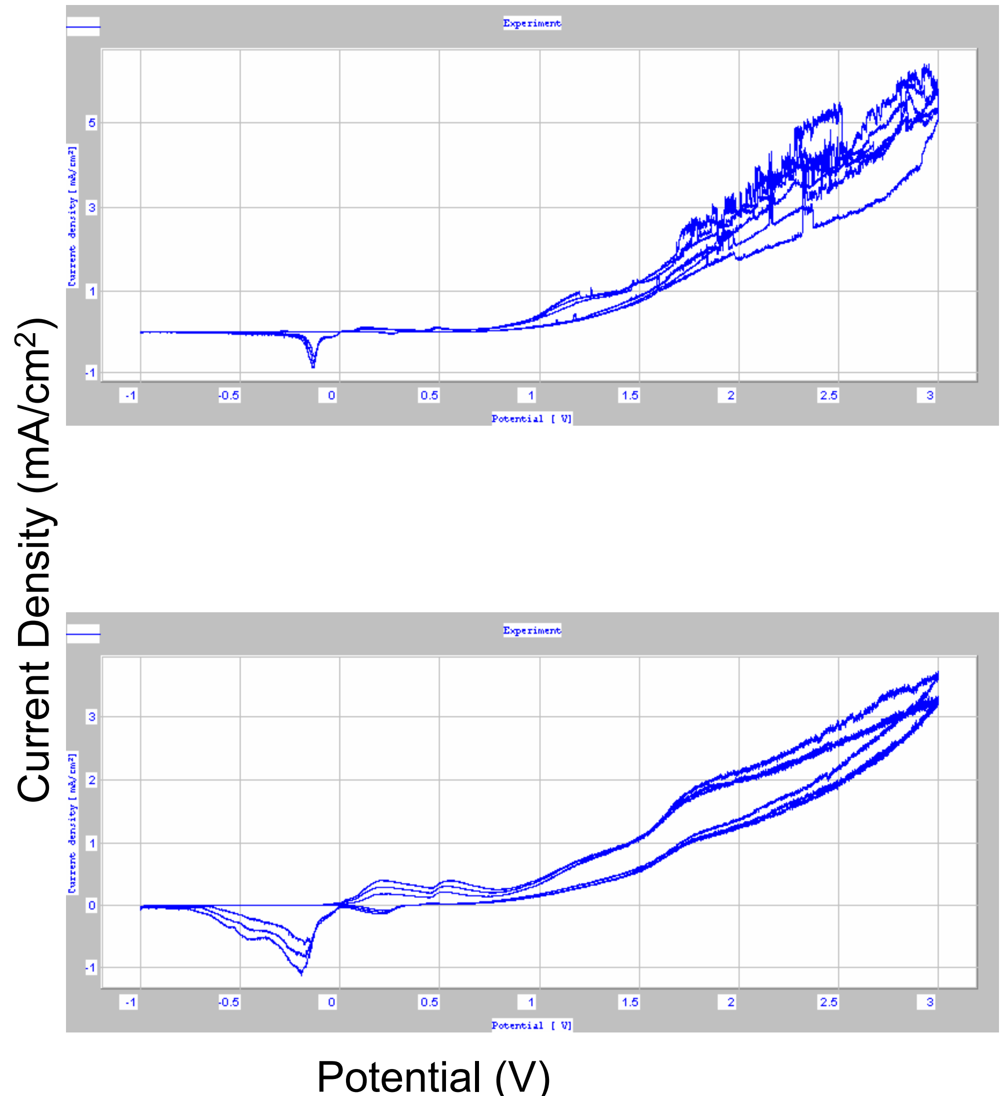


Potential (V)

$TiO_{2-x}N_x$

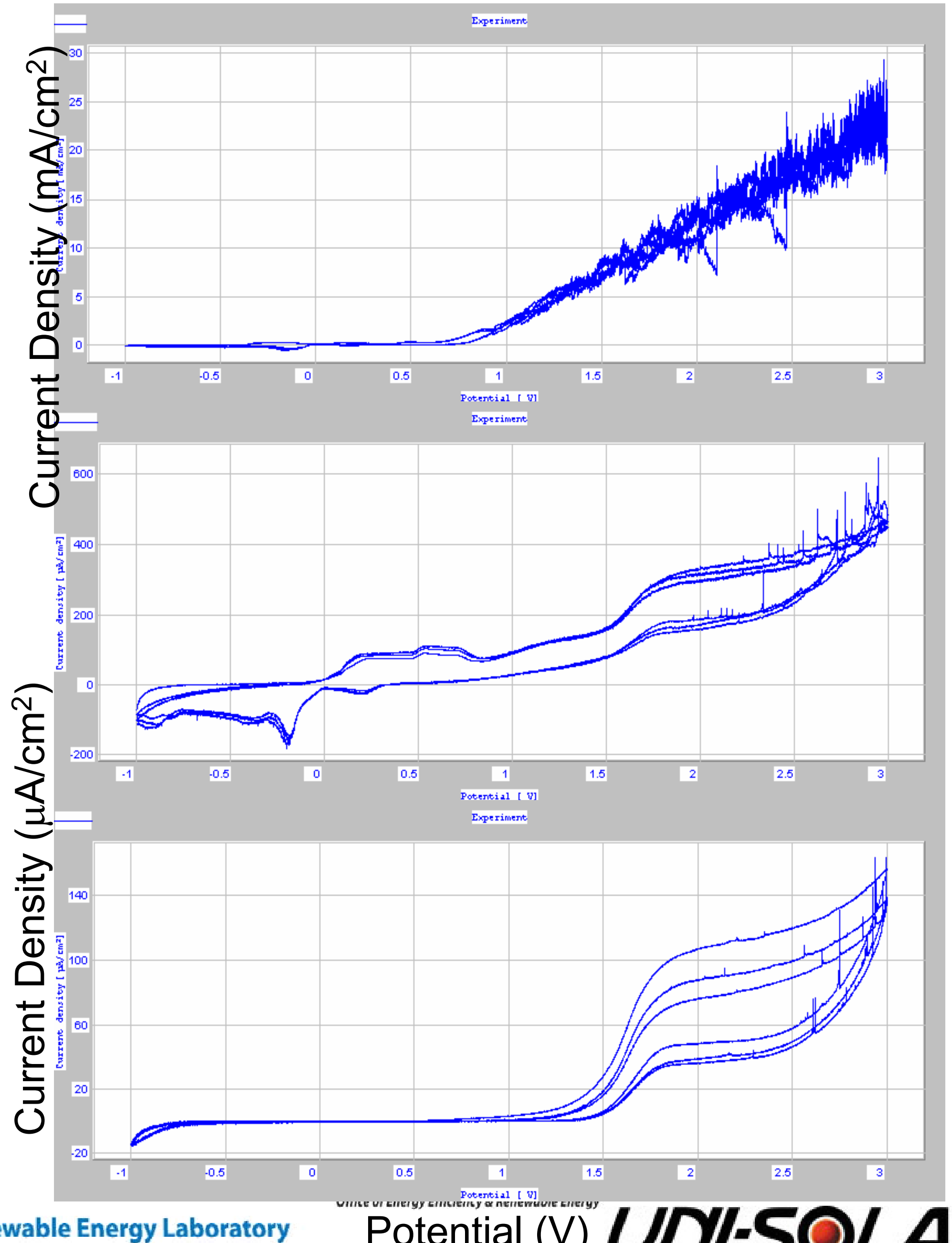
- (Top) Shows higher current density with no annealing, but still stable

- (Bottom) Annealing for 4 hrs, the film remained stable



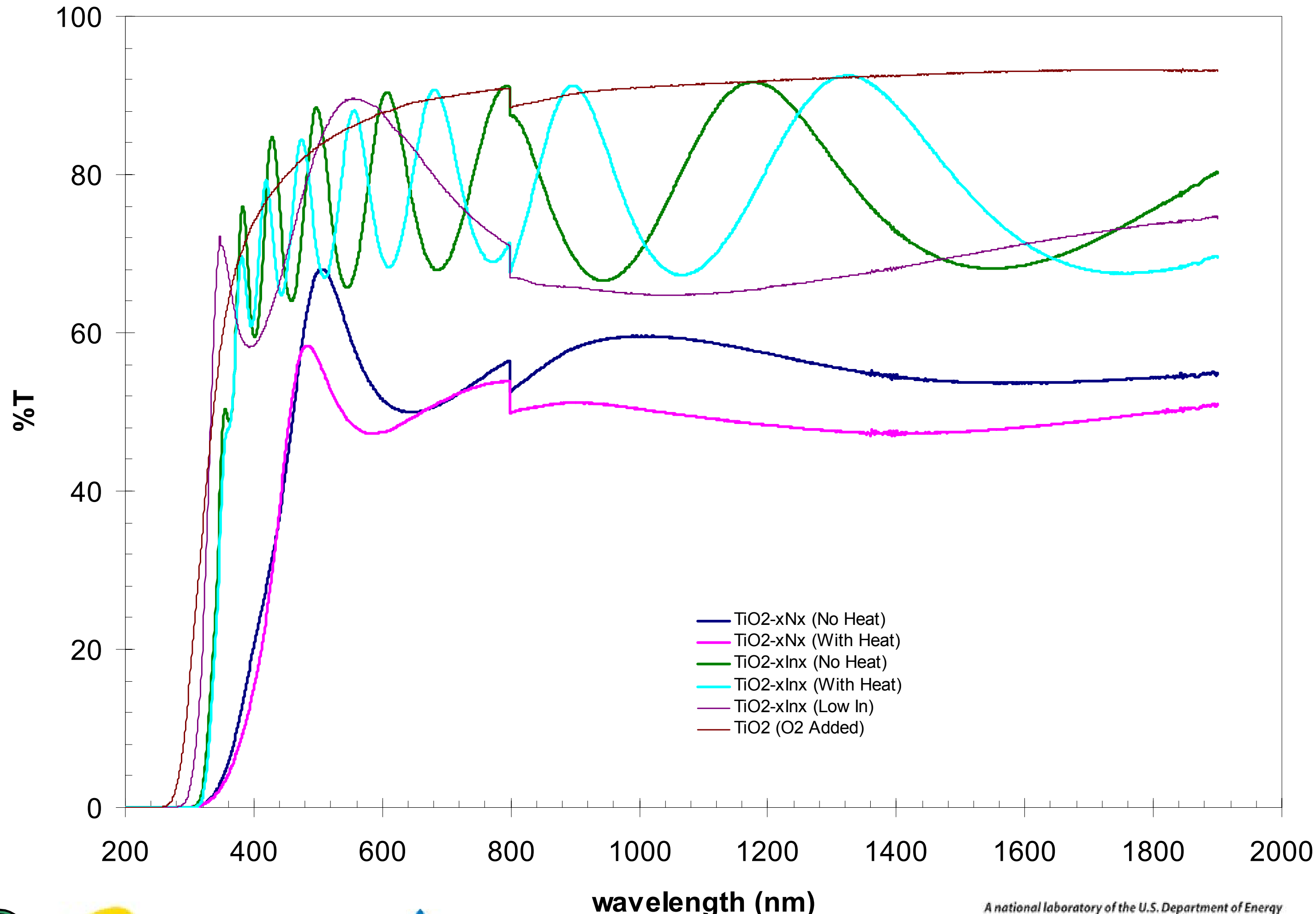
$TiO_{2-x}In_x$

- (Top) Low amounts In dopant showed stability with larger current density
- Whereas (middle) shows lower current density with higher In conc., but still stable
- Photocurrent was observed only with the high levels of In
- For higher In sample, 4hr annealing improves stability of the film



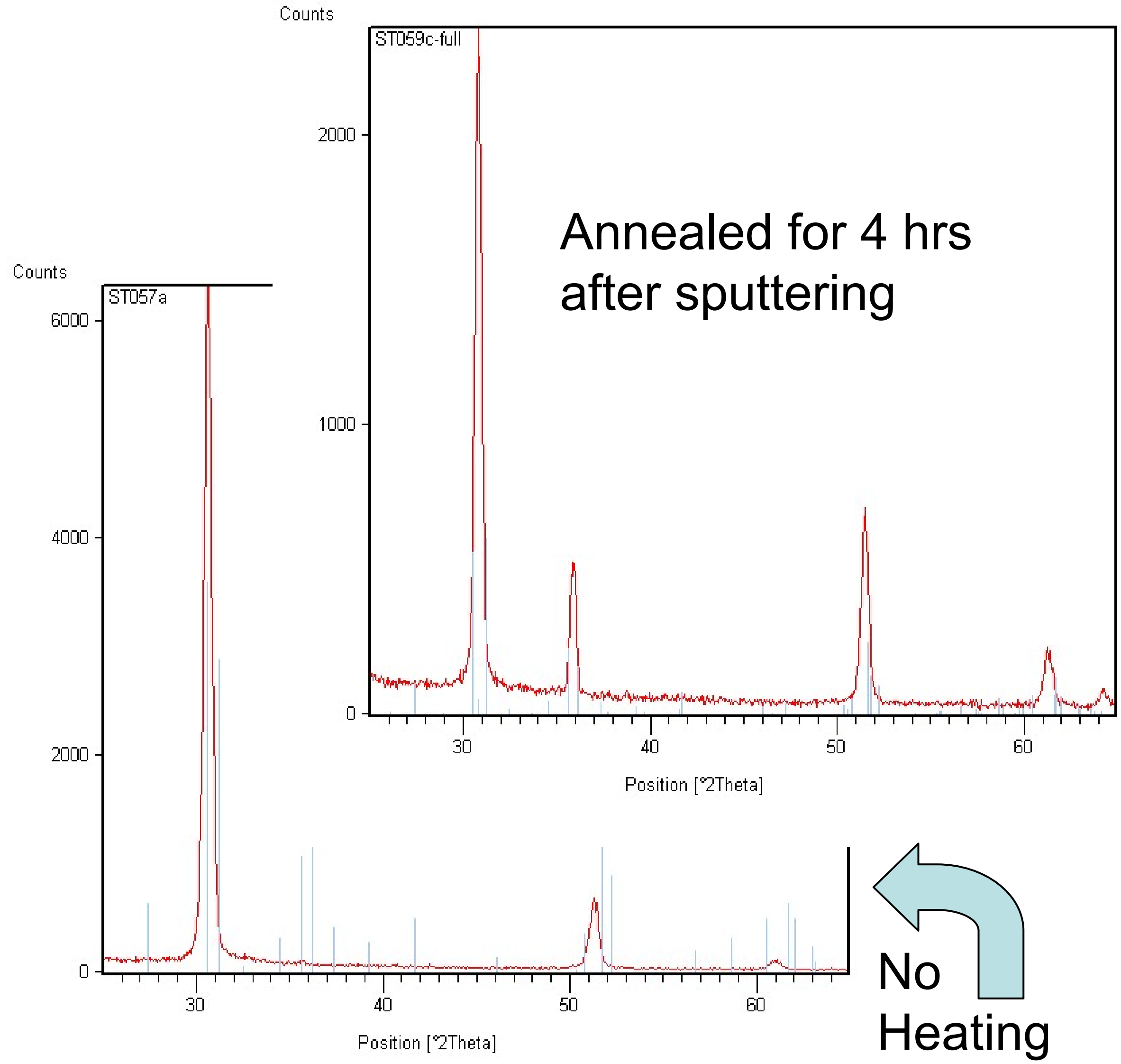
Absorption Spectra for TiO_2

- $TiO_{2-x}In_x$ shows a similar absorption spectra to TiO_2
- $TiO_{2-x}N_x$ shows improved absorption in the visible spectrum



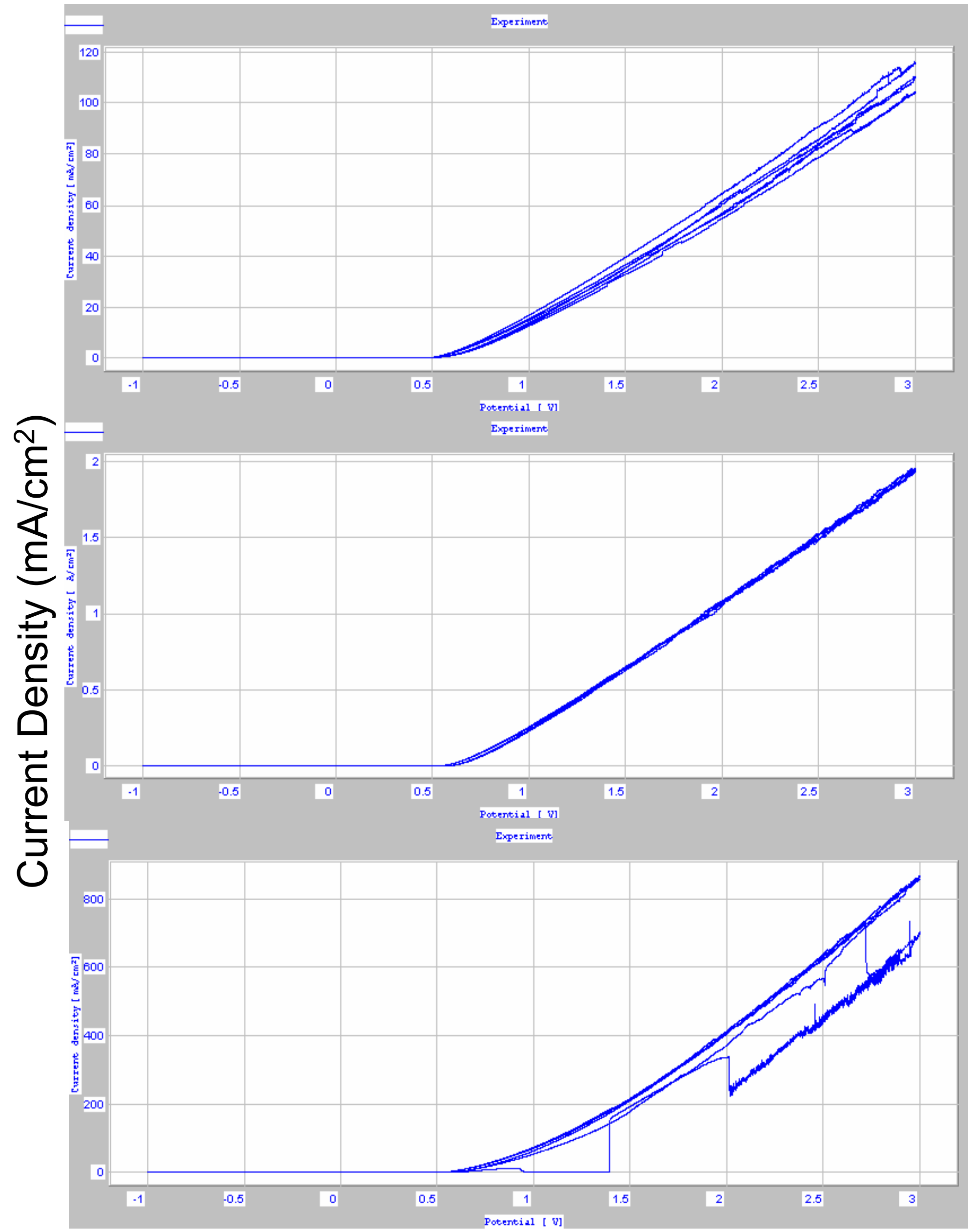
X-ray Diffraction – TiO_2

- $TiO_{2-x}In_x$ exhibited crystallinity, which improved upon heating
- TiO_2 and $TiO_{2-x}N_x$ showed no crystallinity with and without annealing
- Further testing will be performed to identify their structures



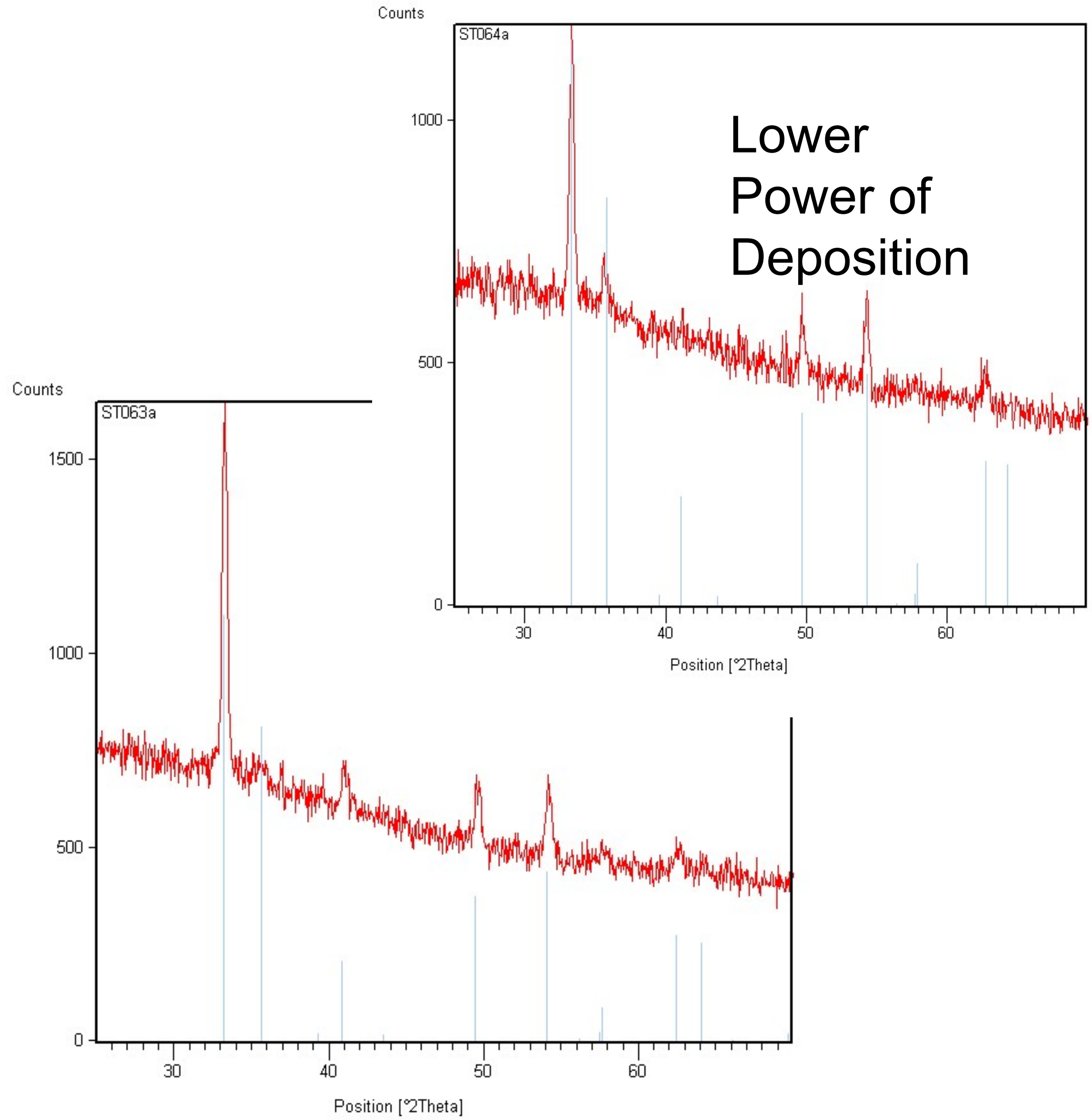
I-V Measurements – Fe_2O_3

- Stable in 33% KOH standard solution
- Initial trials show high current density with excellent stability.
- I-V Curves for Fe_2O_3 made with increasing power (50, 60, & 70 W)
- Lowest power showed minimal instability
- Absorption decreases with increased power used in deposition



X-ray Diffraction – Fe_2O_3

- Fe_2O_3 exhibited crystallinity, which improved upon increased power during deposition
- Scans indicate the presence of hematite only in the films



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Responses to Previous Year Reviewers' Comments

- N/A
- New Project

Future Work

Task 1: Transparent, Conducting and Corrosion Resistant coating for triple-junction tf-Si based photoelectrode

Task 2: Hybrid multijunction PEC electrode having semiconductor-electrolyte junction

Task 3: Understanding and Characterization of photoelectrochemistry

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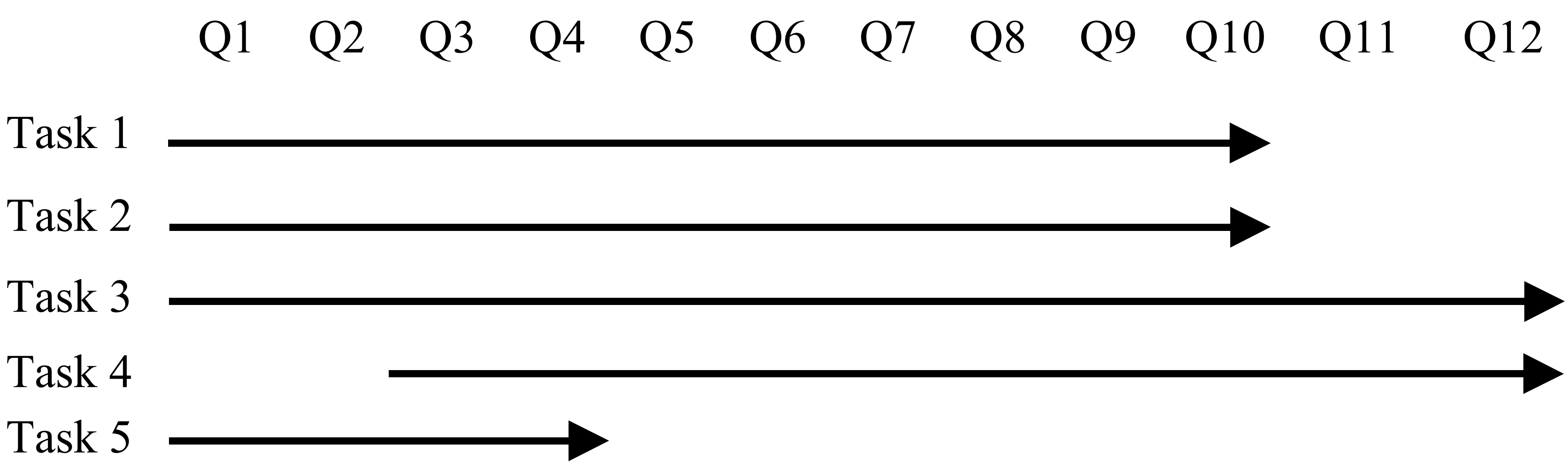

Publications and Presentations

"Development activities toward commercialization of photovoltaic hydrogen systems", Liwei Xu, Presented at Northwest Ohio Alternative Energy Partnership Workshop, University of Toledo Student Union, Oct. 29, 2004.

"Renewable production of hydrogen from water using photoelectrochemical process", Xunming Deng, presented at Purdue University "Hydrogen Economy" Colloquium, March 2, 2005.

Present MWOE's superstrate-type PEC product at the Hydrogen and Fuel Cell Group Exhibit at Hannover Fair, Hannover, Germany, April 11-15, 2005

Demonstrated MWOE's superstrate-type PEC product at COSI-Toledo (Toledo's Science Museum) in its STRANGE MATTER special exhibit, Toledo, Ohio, April 17, 2005.

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- Hydrogen generated from PEC panels needs to be appropriately handled.

Our approach to deal with this hazard is:

- Follow related federal and state guidelines for handling the hydrogen generated in our PEC panels
- Install adequate ventilations
- Provide safety training to all personals handling hydrogen

Other significant hazard related to this research is the handling of hazard gases such as PH_3, GeH_4, SiH_4, BF_3, H_2 during the deposition of semiconductor layers for the photoelectrodes

- Have installed comprehensive safety measures for the handling of toxic gasses including
- toxic gas monitors probing various areas of deposition machines.
- The gas monitor can be accessed remotely and is monitored by police department.
- 24-hour training course has been provided to system operator.
- Visit by Toledo Fire department to discuss various safety issues.

Collaborators

- **Midwest Optoelectronics, LLC**

  Stanley Rubini

- **University of Toledo:**

  Xunming Deng, Alvin Compaan, Robert Collins

  Dean Giolando, Maria Coleman and A.H. Jayatissa

- **National Renewable Energy Laboratory**

  John Turner

- **United Solar Ovonic Corp.**

  Jeffrey Yang